Entropy flux relation for viscoelastic bodies

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Abstract. Thermodynamic restrictions of elastic materials in general are well-known based on the Clausius-Duhem inequality by employing the simple Coleman-Noll procedure. One of the basic assumptions in this entropy inequality is that the entropy flux is defined as the heat flux divided by the absolute temperature. To avoid this unnecessary and possibly too restrictive assumption, the general entropy inequality has been proposed and its thermodynamic consequences exploited following the Müller-Liu procedure in which supply-free bodies are considered and Lagrange Multipliers are introduced. In this new thermodynamic theory, the entropy flux and heat flux relation identical to the above assumption has not been proved for elastic bodies in general. For isotropic elastic bodies, it was proved by Müller in 1971, using explicit isotropic representations for constitutive functions. Unfortunately, the procedure contains a flaw which was later pointed out, but can not be easily resolved. Although it was shown later that it can be proved by Müller-Liu procedure, it has not been available in the literature. In this paper, we shall establish this result, providing the missing details in the previous proof. The analysis will be carried out for isotropic viscoelastic materials and the case of elastic materials follows as a special case.

Keywords: general entropy inequality, thermodynamics with Lagrange multiplier, entropy flux relation

MSC2000: 74A20, 74B20, 80A17

1. Introduction

Exploitation of entropy principle based on the Clausius-Duhem inequality has been widely adopted in the development of modern continuum thermodynamics following the simple Coleman-Noll procedure [1]. The main assumption, that the entropy flux is defined as the heat flux divided by the absolute temperature, while seeming to be plausible in all classical theories of continuum mechanics, is not particularly well motivated for materials in general. In fact, such an entropy flux and heat flux relation is known to be inconsistent with the results from the kinetic theory of ideal gases and is also found to be inappropriate to account for thermodynamics of diffusion (e.g., see [2, 9, 10]). Therefore, we shall not make this assumptions in the present considerations. Exploitation of the entropy principle based on the general entropy inequality has been proposed by Müller [6, 8] and the method of Lagrange multipliers proposed by Liu [3] greatly facilitates its exploitation procedure.

With the general entropy inequality, Müller first proved that for viscous heat-conducting fluids [7] and isotropic thermoelastic bodies [8], the entropy flux is proportional to the heat flux with the coefficient function (called the *coldness*) depending only on the empirical temperature. This is one of the first attempt to exploit the thermodynamic restriction from the general entropy inequality by direct evaluation with explicit isotropic representations of constitutive functions.[1]

In later development of thermodynamic theories based on the general entropy inequality the method of Lagrange multipliers proposed by Liu [3] has been widely used. We shall refer to it as the *Müller-Liu procedure*. The derivation of the relation between the entropy flux and the heat flux, referred to simply as *entropy flux relation*, is a typical problem in those theories. The problem usually relies on isotropic properties of material bodies with the use of either explicit isotropic representations or the flux relation theorems for isotropic vector functions given in [4]. In this paper, we shall establish the entropy flux relation for isotropic viscoelastic bodies as a new derivation of Müller's result [7, 8]. To the knowledge of the present author, similar results for anisotropic material bodies have not been considered yet.

2. Entropy principle

One of the principal objectives of continuum mechanics is to determine or predict the behavior of a body once the external causes are specified. Mathematically, this amounts to solve initial boundary value problems governed by the balance laws of mass, linear momentum and energy,

$$\begin{aligned} &\dot{\rho} + \rho \operatorname{div} \dot{\boldsymbol{x}} = 0, \\ &\rho\, \ddot{\boldsymbol{x}} - \operatorname{div} T = \rho\, \boldsymbol{b}, \\ &\rho\, \dot{\varepsilon} + \operatorname{div} \boldsymbol{q} - T \cdot \operatorname{grad} \dot{\boldsymbol{x}} = \rho\, r, \end{aligned} \tag{1}$$

when the external supplies $\boldsymbol{b}$ and r are given.

The governing field equations are obtained, for the determination of the fields of the density $\rho(\boldsymbol{X}, t)$, the motion $\chi(\boldsymbol{X}, t)$, and the temperature $\theta(\boldsymbol{X}, t)$, after introducing the constitutive relations for the stress T, the internal energy ε, and the heat flux $\boldsymbol{q}$, into the balance laws. Any solution $\{\rho(\boldsymbol{X}, t), \chi(\boldsymbol{X}, t), \theta(\boldsymbol{X}, t)\}$ of the field equations is called a *thermodynamic process*.

[1] Unfortunately, there is a flaw in the proof due to redundant elements in the representation of an isotropic tensor-valued function, see [4, 9].

On the other hand, the behavior of a body must also obey the second law of thermodynamics, *i.e.*, a thermodynamic process must also satisfy the entropy inequality,

$$\rho\dot{\eta} + \operatorname{div}\boldsymbol{\Phi} - \rho s \geq 0, \tag{2}$$

where η is called the specific entropy density, $\boldsymbol{\Phi}$ the entropy flux and s the external entropy supply density.

Following the idea set forth in the fundamental memoir of Coleman and Noll [1], the second law of thermodynamics plays an essential role in constitutive theories of continuum mechanics.

Entropy principle. *It is required that constitutive relations be such that the entropy inequality is satisfied identically for any thermodynamic process.*

Therefore, like the principle of material objectivity and material symmetry, the entropy principle also imposes restrictions on constitutive functions. To find such restrictions is one of the major tasks in modern continuum thermodynamics.

Remark: Motivated by the results of classical thermostatics, it is often assumed that

$$\boldsymbol{\Phi} = \frac{1}{\theta}\,\boldsymbol{q}, \qquad s = \frac{1}{\theta}\,r, \tag{3}$$

where θ is the *absolute* temperature and (2) becomes known as the *Clausius-Duhem inequality*,

$$\rho\dot{\eta} + \operatorname{div}\frac{\boldsymbol{q}}{\theta} - \rho\,\frac{r}{\theta} \geq 0. \tag{4}$$

For elastic materials in general, the thermodynamic restrictions can easily be obtained by the well-known Coleman-Noll procedure [1].

3. Thermodynamics of viscoelastic materials

We shall now exploit the entropy principle for viscoelastic materials following the Müller-Liu procedure. First of all, Müller proposed that if the body is free of external supplies, the entropy supply must also vanish, which is certainly much weaker than the assumptions $(3)_2$. Since constitutive relations do not depend on the external supplies, in exploiting thermodynamic restrictions it suffices to consider only supply-free bodies.

It is more convenient to use referential description for solid bodies. We have the following balance laws for supply-free bodies,

$$
\begin{aligned}
&\rho = J^{-1}\rho_\kappa, \\
&\rho_\kappa \ddot{\boldsymbol{x}} - \operatorname{Div} T_\kappa = 0, \\
&\rho_\kappa \dot{\varepsilon} + \operatorname{Div} \boldsymbol{q}_\kappa - T_\kappa \cdot \dot{F} = 0,
\end{aligned} \tag{5}
$$

and the entropy inequality,

$$
\rho_\kappa \dot{\eta} + \operatorname{Div} \boldsymbol{\Phi}_\kappa \geq 0, \tag{6}
$$

where F is the deformation gradient and $J = |\det F|$, while $T_\kappa = JTF^{-T}$ and $\boldsymbol{q}_\kappa = JF^{-1}\boldsymbol{q}$ are the Piola–Kirchhoff stress tensor and the material heat flux respectively. In analogy to the material heat flux, the material entropy flux $\boldsymbol{\Phi}_\kappa$ is similarly defined. Div is the divergence operator with respect to the referential coordinates.

The constitutive relations for viscoelastic materials can be written as functions of the state variables $(F, \dot{F}, \theta, \boldsymbol{g}_\kappa)$,

$$
\begin{aligned}
T_\kappa &= \widehat{T}_\kappa(F, \dot{F}, \theta, \boldsymbol{g}_\kappa), \\
\boldsymbol{q}_\kappa &= \widehat{\boldsymbol{q}}_\kappa(F, \dot{F}, \theta, \boldsymbol{g}_\kappa), \\
\varepsilon &= \hat{\varepsilon}\,(F, \dot{F}, \theta, \boldsymbol{g}_\kappa),
\end{aligned}
\qquad
\begin{aligned}
\eta &= \hat{\eta}\,(F, \dot{F}, \theta, \boldsymbol{g}_\kappa), \\
\boldsymbol{\Phi}_\kappa &= \widehat{\boldsymbol{\Phi}}_\kappa(F, \dot{F}, \theta, \boldsymbol{g}_\kappa).
\end{aligned} \tag{7}
$$

where $\boldsymbol{g}_\kappa = \nabla\theta$ and $F = \nabla\chi$ are the gradients in referential coordinates. Meanwhile, θ will be regarded as an *empirical* temperature, which is some convenient measure of hotness (or coldness) of the thermodynamic state.

For the purpose of determining the constitutive restrictions, the regularities of the constitutive functions as well as the state variables are usually assumed to be smooth enough as the contexts require. No specific regularity requirements will be given in the subsequent discussions.

Note that the density field $\rho(\boldsymbol{X}, t)$ is completely determined by the motion $\chi(\boldsymbol{X}, t)$ and the density $\rho_\kappa(\boldsymbol{X})$ in the reference configuration. Therefore, we can define a *thermodynamic process* as a solution $\{\chi(\boldsymbol{X}, t), \theta(\boldsymbol{X}, t)\}$ of the field equations by introducing the constitutive relations for T_κ, $\boldsymbol{q}_\kappa$ and ε into the balance laws $(5)_{2,3}$ of linear momentum and energy.

The entropy principle requires that the entropy inequality (6) must hold for any thermodynamic process $\{\chi(\boldsymbol{X}, t), \theta(\boldsymbol{X}, t)\}$. This requirement can be stated in a different way, namely, the fields that satisfy the entropy inequality are constrained by the requirement that they must be solutions of the field equations. Following Liu [3] we can take care of this requirement by the use of Lagrange multipliers:[2]

Method of Lagrange multipliers. *There exist Lagrange multipliers Λ^v and Λ^ε, depending on the state variables, such that the inequality*

$$\rho_\kappa \dot\eta + \operatorname{Div} \boldsymbol{\Phi}_\kappa - \Lambda^v(\rho_\kappa \ddot{\boldsymbol{x}} - \operatorname{Div} T_\kappa) - \Lambda^\varepsilon(\rho_\kappa \dot\varepsilon + \operatorname{Div} \boldsymbol{q}_\kappa - T_\kappa \cdot \dot F) \geq 0 \qquad (8)$$

is valid under no constraints, i.e., valid for any fields $\{\chi(\boldsymbol{X}, t), \theta(\boldsymbol{X}, t)\}$.

Note that after introducing the constitutive relations (7) into (8), the inequality assumes the following form:

$$\sum_a S_a \cdot X_a + \sigma \geq 0, \qquad (9)$$

where $X_a = (\dot\theta, \ddot\chi, \nabla\dot\theta, \nabla\ddot\chi, \nabla(\nabla\theta), \nabla(\nabla\chi), \nabla(\nabla\dot\chi))$, while S_a and σ are functions of $(\theta, \nabla\theta, \nabla\chi, \nabla\dot\chi)$. Here, we use the notation, $\nabla F = \nabla(\nabla\chi)$, to emphasize the symmetry of the second gradient.

Since the inequality (9) must hold for any $\chi(\boldsymbol{X}, t)$ and $\theta(\boldsymbol{X}, t)$, the values of $(\theta, \nabla\theta, \nabla\chi, \nabla\dot\chi)$ and $(\dot\theta, \ddot\chi, \nabla\dot\theta, \nabla\ddot\chi, \nabla(\nabla\theta), \nabla(\nabla\chi), \nabla(\nabla\dot\chi))$ in (9) can be arbitrarily given at any point and any instant.

Note that the inequality (9) is linear in X_a, and the values of X_a can be given independently of the values of S_a and σ. This implies that S_a (respecting the part involved with the symmetry of the second gradients in the corresponding X_a) must vanish, otherwise, it is possible to choose some values of X_a such that the inequality is violated.

First of all, from (8), we note that the coefficient of $\ddot\chi$ is $\rho_\kappa \Lambda^v$, therefore, we conclude that

$$\Lambda^v = 0,$$

and the inequality (8) becomes

$$\rho_\kappa(\dot\eta - \Lambda^\varepsilon \dot\varepsilon) + (\operatorname{Div} \boldsymbol{\Phi}_\kappa - \Lambda^\varepsilon \operatorname{Div} \boldsymbol{q}_\kappa) + \Lambda^\varepsilon T_\kappa \cdot \dot F \geq 0. \qquad (10)$$

Since both η and ε are functions of $(F, \dot F, \theta, \nabla\theta)$, we can write

$$\rho_\kappa(\dot\eta - \Lambda^\varepsilon \dot\varepsilon) = H_\theta\, \dot\theta + H_g \cdot \nabla\dot\theta + H_F \cdot \dot F + H_{\dot F} \cdot \ddot F,$$

where H_θ, H_g, H_F, and $H_{\dot F}$ are functions of $(F, \dot F, \theta, \nabla\theta)$. The linearity of the inequality (10) in $(\dot\theta, \nabla\dot\theta, \ddot F)$ then leads to

$$H_\theta = 0, \qquad H_g = 0, \qquad H_{\dot F} = 0. \qquad (11)$$

[2] For general information on the applicability of the method of Lagrange multipliers, please refer to [3] or Chap. 7 of [5].

The inequality (10) now reduces to

$$\operatorname{Div} \boldsymbol{\Phi}_\kappa - \Lambda^\varepsilon \operatorname{Div} \boldsymbol{q}_\kappa + (H_F + \Lambda^\varepsilon T_\kappa) \cdot \dot{F} \geq 0,$$

which after introducing the constitutive function (7) can be written in the form,

$$\Big(\frac{\partial \widehat{\boldsymbol{\Phi}}_\kappa}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \widehat{\boldsymbol{q}}_\kappa}{\partial \theta}\Big) \cdot \boldsymbol{g}_\kappa + (H_F + \Lambda^\varepsilon T_\kappa) \cdot \dot{F} \\ + G \cdot \nabla(\nabla\theta) + M \cdot \nabla(\nabla\chi) + N \cdot \nabla(\nabla\dot{\chi}) \geq 0,$$

where in component forms,

$$G_{\alpha\beta} = \frac{\partial \hat{\Phi}_\alpha}{\partial \theta_{,\beta}} - \Lambda^\varepsilon \frac{\partial \hat{q}_\alpha}{\partial \theta_{,\beta}}, \; M^i_{\alpha\beta} = \frac{\partial \hat{\Phi}_\alpha}{\partial \chi^i_{,\beta}} - \Lambda^\varepsilon \frac{\partial \hat{q}_\alpha}{\partial \chi^i_{,\beta}}, \; N^i_{\alpha\beta} = \frac{\partial \hat{\Phi}_\alpha}{\partial \dot{\chi}^i_{,\beta}} - \Lambda^\varepsilon \frac{\partial \hat{q}_\alpha}{\partial \dot{\chi}^i_{,\beta}}.$$

By the linearity in $\nabla(\nabla\theta)$, $\nabla(\nabla\chi)$, and $\nabla(\nabla\dot{\chi})$, and the symmetry of the second gradients, the symmetric parts of the coefficients must vanish,

$$G_{\alpha\beta} + G_{\beta\alpha} = 0, \qquad M^i_{\alpha\beta} + M^i_{\beta\alpha} = 0, \qquad N^i_{\alpha\beta} + N^i_{\beta\alpha} = 0. \tag{12}$$

We shall prove further that $M^i_{\alpha\beta} = 0$ and $N^i_{\alpha\beta} = 0$. In order to do this, we need to invoke the *condition of material objectivity*, which implies the following reduced constitutive equations for viscoelastic materials,

$$\boldsymbol{q}_\kappa = \widetilde{\boldsymbol{q}}_\kappa(C, \dot{C}, \theta, \boldsymbol{g}_\kappa), \qquad \boldsymbol{\Phi}_\kappa = \widetilde{\boldsymbol{\Phi}}_\kappa(C, \dot{C}, \theta, \boldsymbol{g}_\kappa), \tag{13}$$

where $C = F^T F$ is the right Cauchy-Green tensor (see e.g. [5, 8, 11]).

On the other hand, since $\dot{C} = \dot{F}^T F + F^T \dot{F}$, we have, for any tensor A,

$$\frac{\partial \widehat{\boldsymbol{q}}_\kappa}{\partial \dot{F}}[A] = \frac{d}{dt} \widehat{\boldsymbol{q}}_\kappa(F, \dot{F} + tA, \theta, \boldsymbol{g}_\kappa)\Big|_{t=0} = \frac{\partial \widetilde{\boldsymbol{q}}_\kappa}{\partial \dot{C}}[A^T F + F^T A].$$

Since $\dot{C}$ is symmetric and accordingly the gradient must be symmetrized. We shall write the gradient after being symmetrized in components simply as

$$\frac{\partial \widetilde{q}_\alpha}{\partial \dot{C}_{\beta\gamma}} \qquad \text{for} \qquad \frac{1}{2}\Big(\frac{\partial \widetilde{q}_\alpha}{\partial \dot{C}_{\beta\gamma}} + \frac{\partial \widetilde{q}_\alpha}{\partial \dot{C}_{\gamma\beta}}\Big),$$

and hence

$$\frac{\partial \widehat{q}_\alpha}{\partial \dot{F}_{i\beta}} = 2\, F^i{}_\gamma \frac{\partial \widetilde{q}_\alpha}{\partial \dot{C}_{\beta\gamma}}.$$

Likewise, similar relations are valid for the material entropy flux $\widehat{\boldsymbol{\Phi}}_\kappa$.

If we define

$$\tilde{N}^{\gamma}_{\alpha\beta} = \frac{\partial \widetilde{\Phi}_{\alpha}}{\partial \dot{C}_{\beta\gamma}} - \Lambda^{\varepsilon} \frac{\partial \widetilde{q}_{\alpha}}{\partial \dot{C}_{\beta\gamma}},$$

then the relation $(12)_3$, $N^i_{\alpha\beta} + N^i_{\beta\alpha} = 0$, becomes

$$F^i{}_{\gamma}(\tilde{N}^{\gamma}_{\alpha\beta} + \tilde{N}^{\gamma}_{\beta\alpha}) = 0.$$

Since F is non-singular, it implies that $\tilde{N}^{\gamma}_{\alpha\beta} = -\tilde{N}^{\gamma}_{\beta\alpha}$, and from the symmetrization of the gradient in $\dot{C}_{\beta\gamma}$, it follows that $\tilde{N}^{\gamma}_{\alpha\beta} = \tilde{N}^{\beta}_{\alpha\gamma}$. Therefore, we have

$$\tilde{N}^{\gamma}_{\alpha\beta} = \tilde{N}^{\beta}_{\alpha\gamma} = -\tilde{N}^{\beta}_{\gamma\alpha} = -\tilde{N}^{\alpha}_{\gamma\beta} = \tilde{N}^{\alpha}_{\beta\gamma} = \tilde{N}^{\gamma}_{\beta\alpha} = -\tilde{N}^{\gamma}_{\alpha\beta},$$

and hence $\tilde{N}^{\gamma}_{\alpha\beta} = 0$, or equivalently, $N^i_{\alpha\beta} = 0$.

Moreover, we also have

$$\frac{\partial \widehat{\boldsymbol{q}}_{\kappa}}{\partial F}[A] = \frac{\partial \widetilde{\boldsymbol{q}}_{\kappa}}{\partial C}[A^T F + F^T A] + \frac{\partial \widetilde{\boldsymbol{q}}_{\kappa}}{\partial \dot{C}}[\dot{F}^T A + A^T \dot{F}],$$

for any tensor A. Since both C and $\dot{C}$ are symmetric, after symmetrizing the gradients, we obtain

$$\frac{\partial \widehat{q}_{\alpha}}{\partial F_{i\beta}} = 2\, F^i{}_{\gamma} \frac{\partial \widetilde{q}_{\alpha}}{\partial C_{\beta\gamma}} + 2\, \dot{F}^i{}_{\gamma} \frac{\partial \widetilde{q}_{\alpha}}{\partial \dot{C}_{\beta\gamma}},$$

and a similar relation for the entropy flux.

Let

$$\tilde{M}^{\gamma}_{\alpha\beta} = \frac{\partial \widetilde{\Phi}_{\alpha}}{\partial C_{\beta\gamma}} - \Lambda^{\varepsilon} \frac{\partial \widetilde{q}_{\alpha}}{\partial C_{\beta\gamma}},$$

then the relation $(12)_2$, $M^i_{\alpha\beta} + M^i_{\beta\alpha} = 0$, becomes

$$F^i{}_{\gamma}(\tilde{M}^{\gamma}_{\alpha\beta} + \tilde{M}^{\gamma}_{\beta\alpha}) + \dot{F}^i{}_{\gamma}(\tilde{N}^{\gamma}_{\alpha\beta} + \tilde{N}^{\gamma}_{\beta\alpha}) = 0,$$

which leads to $F^i{}_{\gamma}(\tilde{M}^{\gamma}_{\alpha\beta} + \tilde{M}^{\gamma}_{\beta\alpha}) = 0$, because $\tilde{N}^{\gamma}_{\alpha\beta} = 0$.

By the same arguments, it also follows that $M^i_{\alpha\beta} = 0$. Therefore, we have

$$\frac{\partial \widetilde{\boldsymbol{\Phi}}_{\kappa}}{\partial C} - \Lambda^{\varepsilon} \frac{\partial \widetilde{\boldsymbol{q}}_{\kappa}}{\partial C} = 0 \qquad \frac{\partial \widetilde{\boldsymbol{\Phi}}_{\kappa}}{\partial \dot{C}} - \Lambda^{\varepsilon} \frac{\partial \widetilde{\boldsymbol{q}}_{\kappa}}{\partial \dot{C}} = 0. \tag{14}$$

Summary of thermodynamic restrictions

The restrictions imposed by the entropy principle on viscoelastic materials in the above exploitation can be summarized below.

The inequality of (8) has been reduced finally to the remaining one, which gives the entropy production density σ as

$$\sigma = \Big(\frac{\partial \widehat{\boldsymbol{\Phi}}_\kappa}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \widehat{\boldsymbol{q}}_\kappa}{\partial \theta}\Big) \cdot \boldsymbol{g}_\kappa + \rho_\kappa \Big(\frac{\partial \eta}{\partial F} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial F} + \frac{1}{\rho_\kappa} \Lambda^\varepsilon T_\kappa\Big) \cdot \dot{F} \geq 0. \quad (15)$$

The material entropy flux and heat flux must satisfy the relations $(12)_1$ and (14), which can now be written as

$$\frac{\partial \widehat{\boldsymbol{\Phi}}_\kappa}{\partial F} = \Lambda^\varepsilon \frac{\partial \widehat{\boldsymbol{q}}_\kappa}{\partial F}, \quad \frac{\partial \widehat{\boldsymbol{\Phi}}_\kappa}{\partial \dot{F}} = \Lambda^\varepsilon \frac{\partial \widehat{\boldsymbol{q}}_\kappa}{\partial \dot{F}}, \quad \Big(\frac{\partial \widehat{\boldsymbol{\Phi}}_\kappa}{\partial \widehat{\boldsymbol{g}}_\kappa}\Big)_{\text{sym}} = \Lambda^\varepsilon \Big(\frac{\partial \widehat{\boldsymbol{q}}_\kappa}{\partial \boldsymbol{g}_\kappa}\Big)_{\text{sym}}, \quad (16)$$

where $(A)_{\text{sym}}$ denotes the symmetric part of the tensor A. Finally, the relations (11) can be written explicitly as

$$\frac{\partial \eta}{\partial \theta} = \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \theta}, \qquad \frac{\partial \eta}{\partial \boldsymbol{g}_\kappa} = \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \boldsymbol{g}_\kappa}, \qquad \frac{\partial \eta}{\partial \dot{F}} = \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \dot{F}}. \quad (17)$$

The relations (15), (16) and (17) are the thermodynamic restrictions for viscoelastic bodies in general. Note that these relations contain one remaining Lagrange multiplier Λ^ε, which depends on $(F, \dot{F}, \theta, \boldsymbol{g}_\kappa)$. Further reductions will be considered in the next sections.

Remark: The relations (16) seem to suggest that the following entropy flux relation,

$$\boldsymbol{\Phi}_\kappa = \Lambda^\varepsilon \boldsymbol{q}_\kappa \quad (18)$$

might be valid. Unfortunately, a rigorous proof has not been available for viscoelastic bodies as well as elastic bodies in general.

However, there is an important property associated with the above entropy flux relation. Suppose that the entropy flux relation (18) is valid for each of the two bodies I and II in thermal contact, then at the contact surface (the wall) the normal components of the heat flux and the entropy flux are continuous,

$$\boldsymbol{q}^I_\kappa \cdot \boldsymbol{n}_\kappa = \boldsymbol{q}^{II}_\kappa \cdot \boldsymbol{n}_\kappa, \qquad \boldsymbol{\Phi}^I_\kappa \cdot \boldsymbol{n}_\kappa = \boldsymbol{\Phi}^{II}_\kappa \cdot \boldsymbol{n}_\kappa,$$

where $\boldsymbol{n}_\kappa$ is the unit normal at the wall. Since from the relation (18),

$$\boldsymbol{\Phi}^I_\kappa = \Lambda^{\varepsilon I} \boldsymbol{q}^I_\kappa, \qquad \boldsymbol{\Phi}^{II}_\kappa = \Lambda^{\varepsilon II} \boldsymbol{q}^{II}_\kappa,$$

it follows that the Lagrange multiplier Λ^ε is continuous across the wall,

$$\Lambda^{\varepsilon I} = \Lambda^{\varepsilon II}.$$

This continuity property duely suggests that the Lagrange multiplier Λ^ε be interpreted as a measure of *thermodynamic* temperature. It is referred to as the *coldness* by Müller [8].

4. Isotropic viscoelastic bodies

For further evaluations of the consequences of the entropy principle, we shall prove the entropy flux relation (18) for isotropic viscoelastic bodies.

For isotropic viscoelastic bodies, the material symmetry condition for the material heat fluxes $\boldsymbol{q}_\kappa$ can be expressed as (see e.g. [5]),

$$\widetilde{\boldsymbol{q}}_\kappa(QCQ^T, Q\dot{C}Q^T, \theta, Q\boldsymbol{g}_\kappa) = Q\,\widetilde{\boldsymbol{q}}_\kappa(C, \dot{C}, \theta, \boldsymbol{g}_\kappa), \qquad \forall\, Q \in \mathcal{O}, \tag{19}$$

where $\mathcal{O}$ is the full orthogonal group. In other words, it is an isotropic vector-valued function of $(C, \dot{C}, \theta, \boldsymbol{g}_\kappa)$.

An isotropic function is restricted in its dependence on the independent variables. Here, instead of using the explicit representation theorems, we shall consider restrictions in the form of differential equations. We need the following lemma:

Lemma. *Let $\mathcal{F}(A)$ be a scalar-valued function of a tensor variable and suppose that $\mathcal{F}(Q) = 0$ for any orthogonal $Q \in \mathcal{O}$. Then the gradient of $\mathcal{F}(A)$ at the identity tensor is symmetric, i.e., for any skew symmetric tensor W,*

$$\nabla_A \mathcal{F}(1) \cdot W = 0. \tag{20}$$

For the proof, just take $Q(t) = \exp tW$, and differentiate $\mathcal{F}(Q(t))$ with respect to t at $t = 0$, (see also [4]).

Entropy flux relation

For the material heat flux $\boldsymbol{q}_\kappa = \widetilde{\boldsymbol{q}}_\kappa(C, \dot{C}, \theta, \boldsymbol{g}_\kappa)$, let us consider, for any constant vector $\boldsymbol{a}$,

$$\mathcal{F}(A) = \boldsymbol{a} \cdot (\widetilde{\boldsymbol{q}}_\kappa(ACA^T, A\dot{C}A^T, \theta, A\boldsymbol{g}_\kappa) - A\,\widetilde{\boldsymbol{q}}_\kappa(C, \dot{C}, \theta, \boldsymbol{g}_\kappa)).$$

Then from the condition (19), it follows that $\mathcal{F}(Q) = 0$ for any $Q \in \mathcal{O}$ and hence the above Lemma implies that

$$\begin{aligned}\nabla_A \mathcal{F}(1) \cdot W &= 0 \\ &= \boldsymbol{a} \cdot \Big(\frac{\partial \widetilde{\boldsymbol{q}}_\kappa}{\partial C}[WC - CW] + \frac{\partial \widetilde{\boldsymbol{q}}_\kappa}{\partial \dot{C}}[W\dot{C} - \dot{C}W] + \frac{\partial \widetilde{\boldsymbol{q}}_\kappa}{\partial \boldsymbol{g}_\kappa} W\boldsymbol{g}_\kappa - W\widetilde{\boldsymbol{q}}_\kappa\Big).\end{aligned}$$

In analogy, we have a similar equation for the material entropy flux $\boldsymbol{\Phi}_\kappa = \widetilde{\boldsymbol{\Phi}}_\kappa(C, \dot{C}, \theta, \boldsymbol{g}_\kappa)$.

Now, let $\boldsymbol{k} = \boldsymbol{\Phi}_\kappa - \Lambda^\varepsilon \boldsymbol{q}_\kappa$. From the above relations for both $\widetilde{\boldsymbol{\Phi}}_\kappa$ and $\widetilde{\boldsymbol{q}}_\kappa$, and the relation (14), we have

$$\boldsymbol{a} \cdot W\boldsymbol{k} = \boldsymbol{a} \cdot \widetilde{G} W \boldsymbol{g}_\kappa, \tag{21}$$

where

$$\widetilde{G} = \frac{\partial \widetilde{\boldsymbol{\Phi}}_\kappa}{\partial \boldsymbol{g}_\kappa} - \Lambda^\varepsilon \frac{\partial \widetilde{\boldsymbol{q}}_\kappa}{\partial \boldsymbol{g}_\kappa}.$$

Since it holds for any vector $\boldsymbol{a}$ and any skew symmetric tensor W, in particular, by taking alternatively,

$$\begin{aligned} \boldsymbol{a} &= \boldsymbol{e}_1, \qquad W = \boldsymbol{e}_2 \otimes \boldsymbol{e}_3 - \boldsymbol{e}_3 \otimes \boldsymbol{e}_2, \\ \boldsymbol{a} &= \boldsymbol{e}_2, \qquad W = \boldsymbol{e}_3 \otimes \boldsymbol{e}_1 - \boldsymbol{e}_1 \otimes \boldsymbol{e}_3, \\ \boldsymbol{a} &= \boldsymbol{e}_3, \qquad W = \boldsymbol{e}_1 \otimes \boldsymbol{e}_2 - \boldsymbol{e}_2 \otimes \boldsymbol{e}_1, \end{aligned}$$

and knowing from $(12)_1$ that $\widetilde{G}$ is skew symmetric, we obtain

$$\widetilde{G}_{12} g_3 + \widetilde{G}_{31} g_2 = 0, \qquad \widetilde{G}_{23} g_1 + \widetilde{G}_{12} g_3 = 0, \qquad \widetilde{G}_{31} g_2 + \widetilde{G}_{23} g_1 = 0.$$

Summing of the last three equations gives $\widetilde{G}_{12} g_3 + \widetilde{G}_{23} g_1 + \widetilde{G}_{31} g_2 = 0$, which implies immediately that

$$\widetilde{G}_{12} g_3 = 0, \qquad \widetilde{G}_{23} g_1 = 0, \qquad \widetilde{G}_{31} g_2 = 0.$$

Since $\boldsymbol{g}_\kappa = (g_1, g_2, g_3)$ does not vanish in general, it follows that $\widetilde{G}_{12} = \widetilde{G}_{23} = \widetilde{G}_{31} = 0$ or the skew symmetric tensor $\widetilde{G} = 0$. Therefore, by (21), since W and $\boldsymbol{a}$ are arbitrary, $\boldsymbol{k}$ must vanish and we have proved the entropy flux relation,

$$\boldsymbol{\Phi}_\kappa = \Lambda^\varepsilon \boldsymbol{q}_\kappa. \tag{22}$$

The absolute temperature

Taking the gradient of (22) with respect to $\boldsymbol{g}_\kappa$ and using again the relation $(16)_3$, we obtain

$$\frac{\partial \Lambda^\varepsilon}{\partial \boldsymbol{g}_\kappa} \cdot \boldsymbol{q}_\kappa = \operatorname{tr}\Big(\frac{\partial \boldsymbol{\Phi}_\kappa}{\partial \boldsymbol{g}_\kappa} - \Lambda^\varepsilon \frac{\partial \boldsymbol{q}_\kappa}{\partial \boldsymbol{g}_\kappa} \Big) = 0,$$

from which it implies that Λ^ε must be independent of $\boldsymbol{g}_\kappa$, since $\boldsymbol{q}_\kappa$ does not vanish in general. Similarly, by taking the gradient with respect to F and $\dot{F}$ respectively and using the relation $(16)_{1,2}$, it follows immediately that Λ^ε must be independent of F and $\dot{F}$. Therefore, we have

$$\Lambda^\varepsilon = \Lambda(\theta),$$

and the entropy production density (15) becomes

$$\sigma = \frac{\partial \Lambda}{\partial \theta} (\boldsymbol{q}_\kappa \cdot \boldsymbol{g}_\kappa) - \Lambda \Big(\rho_\kappa \frac{\partial \psi}{\partial F} - T_\kappa \Big) \cdot \dot{F} \geq 0, \tag{23}$$

where $\psi = \varepsilon - \Lambda^{-1}\eta$.

Since the entropy production should not vanish in the presence of temperature gradient in time-independent processes, we shall require that $\partial\Lambda/\partial\theta \neq 0$. Consequently, $\Lambda(\theta)$ depends monotonically on θ and hence $\Lambda(\theta)$ can also be taken as a temperature measure referred to as the *coldness*.

On the other hand, we can summarize the relations (17) in the following differential form,

$$d\eta = \Lambda\, d\varepsilon + \Big(\frac{\partial\eta}{\partial F} - \Lambda\frac{\partial\varepsilon}{\partial F}\Big)\cdot dF = \Lambda\Big(d\varepsilon - \frac{\partial\psi}{\partial F}\cdot dF\Big). \tag{24}$$

By comparison with the classical Gibbs relation in thermostatics, we can now identify the coldness Λ as the reciprocal of the *absolute temperature*. Moreover, the empirical temperature θ could have been taken at the outset to be the absolute temperature, i.e., we have

$$\Lambda^{\varepsilon}(\theta) = \frac{1}{\theta}. \tag{25}$$

Therefore, ψ is the free energy function $\psi = \varepsilon - \theta\eta$. From $(17)_{2,3}$ it is independent of $(\boldsymbol{g}_\kappa, \dot F)$,

$$\psi = \psi(F,\theta),$$

and the relation $(17)_1$ implies that

$$\frac{\partial\psi}{\partial\theta} = -\eta.$$

Consequently, both internal energy and the entropy densities are functions of (F,θ) only,

$$\varepsilon = \varepsilon(F,\theta), \qquad \eta = \eta(F,\theta).$$

The equilibrium state

A process with no entropy production is said to determine an equilibrium state. From (23), the entropy production density $\sigma(F,\dot F,\theta,\boldsymbol{g}_\kappa)$ is a non-negative quantity,

$$\sigma = -\frac{1}{\theta^2}\,(\boldsymbol{q}_\kappa\cdot\boldsymbol{g}_\kappa) - \frac{1}{\theta}\Big(\rho_\kappa\frac{\partial\psi}{\partial F} - T_\kappa\Big)\cdot\dot F \geq 0,$$

and it attains the minimum, namely zero, at the states such that $g_\kappa = 0$ and $\dot F = 0$,

$$\sigma|_E = \sigma(F,0,\theta,0) = 0.$$

Necessary conditions for a minimum at the equilibrium state require that

$$\frac{\partial \sigma}{\partial \dot{F}}\Big|_E = 0, \qquad \frac{\partial \sigma}{\partial \boldsymbol{g}_\kappa}\Big|_E = 0,$$

which lead to the well-known relation for the (equilibrium) stress, and the vanishing of the heat flux at equilibrium,

$$T_\kappa|_E = \rho_\kappa \frac{\partial \psi}{\partial F}, \qquad \boldsymbol{q}_\kappa|_E = 0.$$

We shall call $T_\kappa|_E$ the *elastic* Piola-Kirchhoff stress and define the *viscous* Piola Kirchhoff stress as

$$S_\kappa = T_\kappa - T_\kappa|_E,$$

so that

$$S_\kappa = \widehat{S}_\kappa(F, \dot{F}, \theta, \boldsymbol{g}_\kappa), \quad \text{and} \quad \widehat{S}_\kappa(F, 0, \theta, 0) = 0,$$

and the remaining entropy inequality becomes

$$-\frac{1}{\theta}\, \boldsymbol{q}_\kappa \cdot \boldsymbol{g}_\kappa + S_\kappa \cdot \dot{F} \geq 0.$$

Moreover, the expression (24) leads to the well-known Gibbs relation,

$$d\eta = \frac{1}{\theta}\Big(d\varepsilon - \frac{1}{\rho_\kappa}\, T_\kappa|_E \cdot dF\Big). \tag{26}$$

We can summarize the above general thermodynamic restrictions in the following proposition:

Proposition. *For isotropic viscoelastic bodies, the Cauchy stress can be expressed as*

$$T = T_E(F, \theta) + S(F, \dot{F}, \theta, \boldsymbol{g}), \qquad S(F, 0, \theta, 0) = 0,$$

where the elastic stress T_E and the viscous stress S, satisfy the following Gibbs relation and the entropy production inequality:

$$d\eta = \frac{1}{\theta}\, \Big(d\varepsilon - \frac{1}{\rho}\, T_E F^{-T} \cdot dF\Big),$$

$$-\frac{1}{\theta}\, \boldsymbol{q} \cdot \boldsymbol{g} + S \cdot \dot{F} F^{-1} \geq 0.$$

In particular, the elastic stress tensor, the internal energy and the entropy are related to the free energy function $\psi = \psi(F, \theta)$ by

$$T_E = \rho \frac{\partial \psi}{\partial F} F^T, \qquad \varepsilon = \psi - \theta \frac{\partial \psi}{\partial \theta}, \qquad \eta = -\frac{\partial \psi}{\partial \theta}. \tag{27}$$

Moreover, the following entropy flux relation is valid,

$$\boldsymbol{\Phi} = \frac{1}{\theta}\, \boldsymbol{q}.$$

5. Isotropic elastic bodies

Following the above exploitation of Müller-Liu procedure for viscoelastic bodies, one can easily see that for isotropic elastic bodies with state variables $(F, \theta, \boldsymbol{g}_\kappa)$, the relations $(16)_{1,3}$ and $(17)_{1,2}$ remain valid, while the relations $(16)_2$ and $(17)_3$ are trivially satisfied. Therefore, the proof of the entropy flux relation (22) for elastic bodies follows as a special case. Therefore, we have

$$\boldsymbol{\Phi}_\kappa = \Lambda^\varepsilon \boldsymbol{q}_\kappa, \qquad \Lambda^\varepsilon = \Lambda^\varepsilon(\theta) = \frac{1}{\theta}.$$

On the other hand, since constitutive functions are independent of $\dot{F}$, its coefficient in the remaining entropy production inequality (15) must vanish, which implies that

$$T_\kappa = \rho_\kappa \frac{\partial \psi}{\partial F} = T_\kappa(F, \theta).$$

In summary, the isotropic elastic bodies can be regarded as a special case of the isotropic viscoelastic bodies with no viscous stress in the above Proposition.

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